CARBON DIOXIDE CAPTURE FROM FLUE GAS USING DRY REGENERABLE SORBENTS

QUARTERLY TECHNICAL PROGRESS REPORT

Reporting Period: April 1, 2003 to June 30, 2003

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DOE Cooperative Agreement No. DE-FC26-00NT40923

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August 2003

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ABSTRACT

This report describes research conducted between April 1, 2003 and June 30, 2003 on the use of dry regenerable sorbents for concentration of carbon dioxide from flue gas. Grade 1 sodium bicarbonate performed similarly to grade 5 sodium bicarbonate in fixed bed testing in that activity improved after the first carbonation cycle and did not decline over the course of 5 cycles. Thermogravimetric analysis indicated that sodium bicarbonate sorbents produced by calcination of sodium bicarbonate are superior to either soda ash or calcined trona. Energy requirements for regeneration of carbon dioxide sorbents (either wet or dry) is of primary importance in establishing the economic feasibility of carbon dioxide capture processes. Recent studies of liquid amine sorption processes were reviewed and found to incorporate conflicting assumptions of energy requirements. Dry sodium based processes have the potential to be less energy intensive and thus less expensive than oxygen inhibited amine based systems. For dry supported sorbents, maximizing the active fraction of the sorbent is of primary importance in developing an economically feasible process.

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1.0 EXECUTIVE SUMMARY

The objective of this project is to develop a simple and inexpensive process to separate CO_2 as an essentially pure stream from a fossil fuel combustion system using a regenerable sorbent. The sorbents being investigated in this project are primarily alkali carbonates, and particularly sodium carbonate and potassium carbonate, which are converted to bicarbonates or intermediate salts through reaction with carbon dioxide and water vapor. Bicarbonates are regenerated to carbonates when heated, producing a nearly pure CO_2 stream after condensation of water vapor.

This quarter, 5-cycle fixed bed reactor testing of grade 1 sodium bicarbonate (SBC#1), confirmed results of previous testing with SBC#3, in that carbonation activity in cycles 2 through 5 was superior to that observed in the first cycle, and that activity did not decline over the first five cycles. TGA testing confirmed that sodium carbonate sorbents produced by calcination of sodium bicarbonate are far more reactive than either natural (low density) soda ash or commercial grade dense soda ash. Two sodium sesquicarbonate (trona) materials were also tested and found to be inferior to calcined SBC as a sorbent.

Analysis of two different conceptual amine-based CO_2 removal systems revealed large differences in assumed process energy requirements. Some additional work will be required to refine the economic comparison between a dry carbonate based sorbent system and liquid absorption system, however, for processes involving dry supported sorbents, active material loading has been identified as a critical variable.

2.0 INTRODUCTION

Fossil fuels used for power generation, transportation, and by industry are the primary source of anthropogenic CO_2 emissions to the atmosphere. Much of the CO_2 emission reduction effort will focus on large point sources, with fossil fuel fired power plants being a prime target. The CO_2 content of power plant flue gas varies from 4% to 9% (vol), depending on the type of fossil fuel used and on operating conditions. Although new power generation concepts that may result in CO_2 control with minimal economic penalty are under development, these concepts are not generally applicable to the large number of existing power plants.

This study is based on the use of a dry, regenerable sorbent to remove CO_2 from flue gases. Sorbent regeneration produces a gas stream containing only CO_2 and H_2O. The H_2O may be separated by condensation to produce a pure CO_2 stream for subsequent use or sequestration. The primary reactions, based upon the use of sodium bicarbonate (SBC) as the sorbent precursor and sodium carbonate as the reaction product are:

$$2NaHCO_3(s) \rightarrow Na_2CO_3(s) + CO_2(g) + H_2O(g) \qquad (1)$$

and

$$Na_2CO_3(s) + CO_2(g) + H_2O(g) \rightarrow 2NaHCO_3(s) \qquad (2)$$

Reaction (1) releases CO_2 and regenerates the sorbent, while Reaction (2) is used to capture CO_2. Several other solid products, intermediate between sodium carbonate and sodium bicarbonate, may also be produced under the anticipated reaction conditions. An intermediate compound, $Na_2CO_3C3NaHCO_3$, known as Wegscheider's salt, forms at the reaction conditions of interest.

Analogous reactions (Reactions 3 and 4) take place within the potassium carbonate system:

$$2KHCO_3(s) \div K_2CO_3(s) + CO_2(g) + H_2O(g) \tag{3}$$

and

$$K_2CO_3(s) + CO_2(g) + H_2O(g) \div 2KHCO_3(s). \tag{4}$$

A compound salt of potassium carbonate and potassium bicarbonate is also thought to be of importance at the conditions of interest.

Trona (sodium sesquicarbonate) can also be used as a sorbent precursor. The following reactions of trona are slightly different from the direct reversible reaction of $NaHCO_3$ (reaction 1). Trona is initially calcined according to:

$$2[Na_2CO_3CNaHCO_3C2H_2O(s)] \div 3Na_2CO_3(s) + CO_2(g) + 5H_2O(g) \tag{5}$$

Subsequent carbonation and calcination reactions proceed according to:

$$Na_2CO_3(s) + CO_2(g) + H_2O(g) \text{ ø } 2NaHCO_3(s) \tag{6}$$

This report describes activities conducted between April 1, 2003 and June 30, 2003 by RTI and its subcontractors Louisiana State University (LSU) and Church and Dwight (C&D). Activities conducted this quarter include fixed bed reactor studies at LSU and thermogravimetric analysis studies (TGA) at RTI. In addition, RTI continued development of mathematical models, and Church and Dwight began work on sizing and costing of equipment.

3.0 EXPERIMENTAL

3.1 Fixed Bed Testing at LSU

One successful 5.5 cycle fixed bed test was completed this quarter using SBC#1 at a nominal carbonation temperature of 60EC. A second 5.5 cycle test was conducted using SBC#3 with calcination in pure CO_2 at 160EC, which produced questionable results in some cases. Test conditions are given in Table 1. Physical properties of these materials were reported previously (Green, et al., 2001).

Table 1. Reaction Conditions For Fixed-bed Test Conducted at LSU.

		First Test	**Second Test**
	Sorbent Precursor	**SBC#1**	**SBC#3**
Calcination	Temperature	120EC	160EC
	Pressure	1 atm	1 atm
	Gas Composition	100% N_2	100% CO_2
Carbonation	Temperature	60EC	60EC
	Pressure	1 atm	1 atm
	Gas Composition	8 mol% CO_2	8 mol% CO_2
		16 mol% H_2O	16 mol% H_2O
		76 mol% N_2	76 mol% N_2
	Gas Flow Rate	150 scc/min	150 scc/min

3.2 Thermogravimetric Analysis (TGA) at RTI

Five materials were tested for carbonation capacity and activity in the TGA this quarter. Four materials were obtained from Church and Dwight: Natural Light Low Density Soda Ash, Natural Sodium Sesquicarbonate (unrefined trona), Sodium carbonate (dense ash), and Commercial Sodium Sesquicarbonate. An additional batch of 40% supported sodium carbonate prepared at RTI this quarter was also tested.

4.0 RESULTS AND DISCUSSION

4.1 Fixed Bed Reactor Testing at LSU

A 5.5 cycle test was conducted to compare the performance of SBC#1 with previous data obtained for SBC#3. CO_2 concentrations as a function of time for the carbonation phase of this test are shown in Figure 1. These results are quite similar to those reported in the previous quarter (Green, et al., 2003) for SBC#3 at the same conditions. Once again, the improved performance in cycles 2 through 5 is evident. Initial outlet CO_2 concentrations during cycles 2 through 5 were in the range of 1.0% to 1.5%, compared to 3.5% in cycle 1. For practical purposes, there is no difference in performance in cycles 2 through 5.

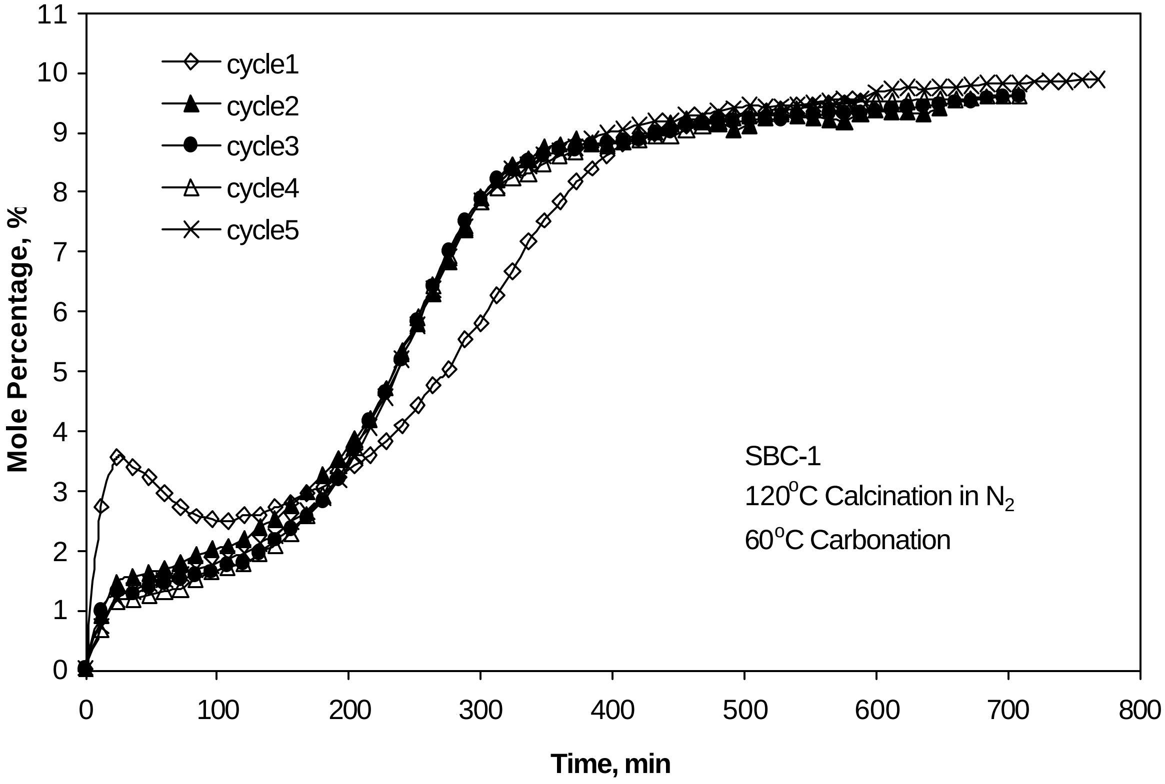

Figure 1. CO_2 concentration versus time for five carbonation cycles using SBC#1 and a nominal 60EC carbonation temperature.

The performance of SBC#1 and SBC#3 is further compared in Figure 2, where percent CO_2 removal in the third gas chromatography sample is shown as a function of cycle number. Figure 2 is based on Figure 5 from the April 2003 quarterly report, with the SBC#1 results at obtained at 60EC added. The third carbonation sample was chosen for the comparison because of scatter in the first two samples as the carbonation feed gas rates and composition reached steady state. For both SBC#1 and SBC#3, the CO_2 removal increased from above 60% in cycle 1 to almost 90% in the remaining cycles.

Figure 3 compares final sorbent conversion, based on Wegscheider's salt product, as a function of cycle number. Data from Figure 6 of the April, 2003 quarterly report have been added and the results have been restated in terms of percent sorbent conversion (instead of cumulative mols of CO_2 removed). The two quantities are proportional to each other. SBC#3 and SBC#1 results at 60EC both show effectively complete sorbent conversion, and they are effectively equal to each other. In contrast the final sorbent conversion for SBC#3 at 70EC is slightly less than 90%.

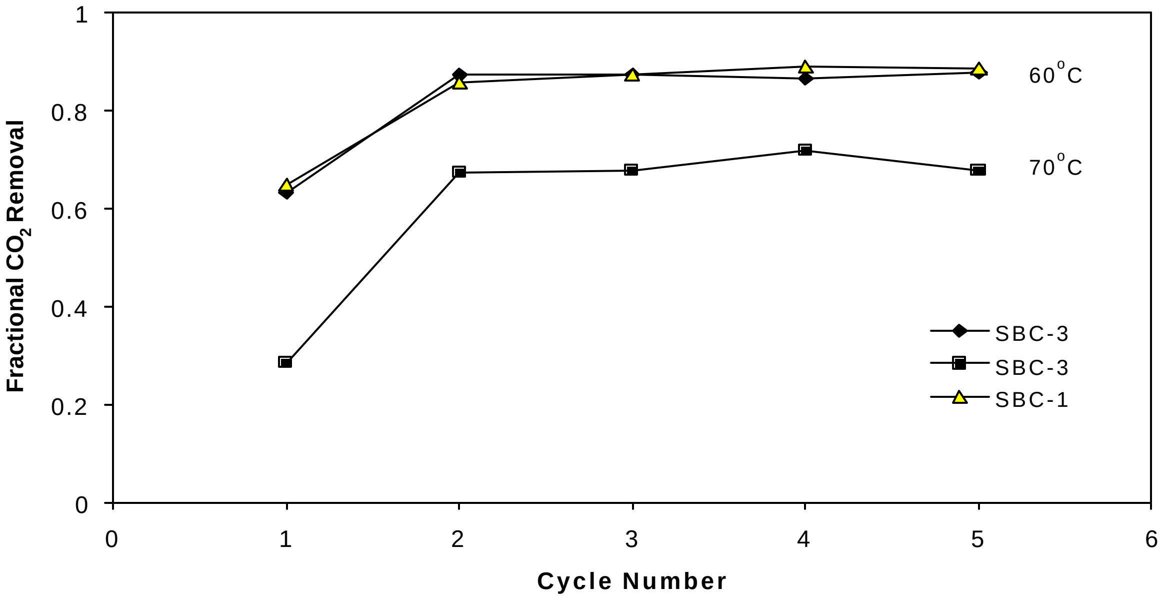

Figure 2. Percent CO_2 removal as a function of cycle number and carbonation temperature for SBC#1 and SBC#3 (based on CO_2 concentration in the third carbonation sample).

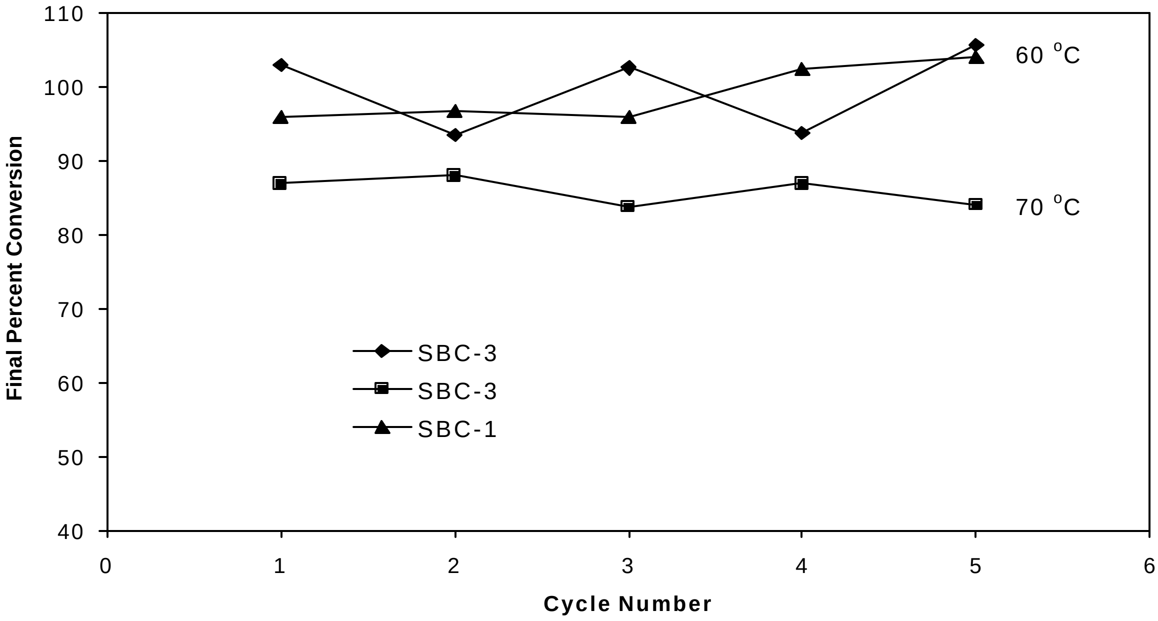

Figure 3. Final percent sorbent conversion to Wegscheider's salt as a function of cycle number and temperature using SBC#1 and SBC#3.

A CO_2 calcination atmosphere at 160EC was used in the second 5.5-cycle run. This provides a closer approach to realistic calcination conditions than the lower temperature N_2 calcination conditions. Selected results are presented below even though they are of questionable reliability. Since it is impossible to follow the progress of the calcination phase by monitoring CO_2 in the product gas, the calcination cycle was continued for a fixed time of 6 hours. Carbonation was then carried out using the standard feed composition of 8% CO_2, 16% H_2O, balance N_2 at a feed rate of 150 scc/min and a nominal temperature of 60EC. The carbonation cycle was also terminated after 6 hours instead of the 10 to 12 hours used in earlier tests (see Figure 1).

Figure 4 shows the mol percent CO_2 (dry basis) in the carbonation product gas as a function of time for each of the five cycles. Several features, in addition to the decreased carbonation time, are immediately evident when comparing Figures 1 and 4. The initial CO_2 concentrations are considerably larger in Figure 4 and there is a significant increase in the data scatter between cycles compared to Figure 1. There is a noticeable improvement in performance between cycles 1 and 2, but performance in cycles 3 and 4 was much like the cycle 1 performance. Cycle 5 results are obviously erroneous since essentially no CO_2 was found in the product gas. This indicates either a malfunction in the analytical system or a leak so severe that essentially no CO_2 reached the reactor. This problem also calls into question the results from the first four cycles. Finally, it is obvious that carbonation was not complete after 6 hours. This also differs from the data of Figure 1 that show almost complete conversion in that time period.

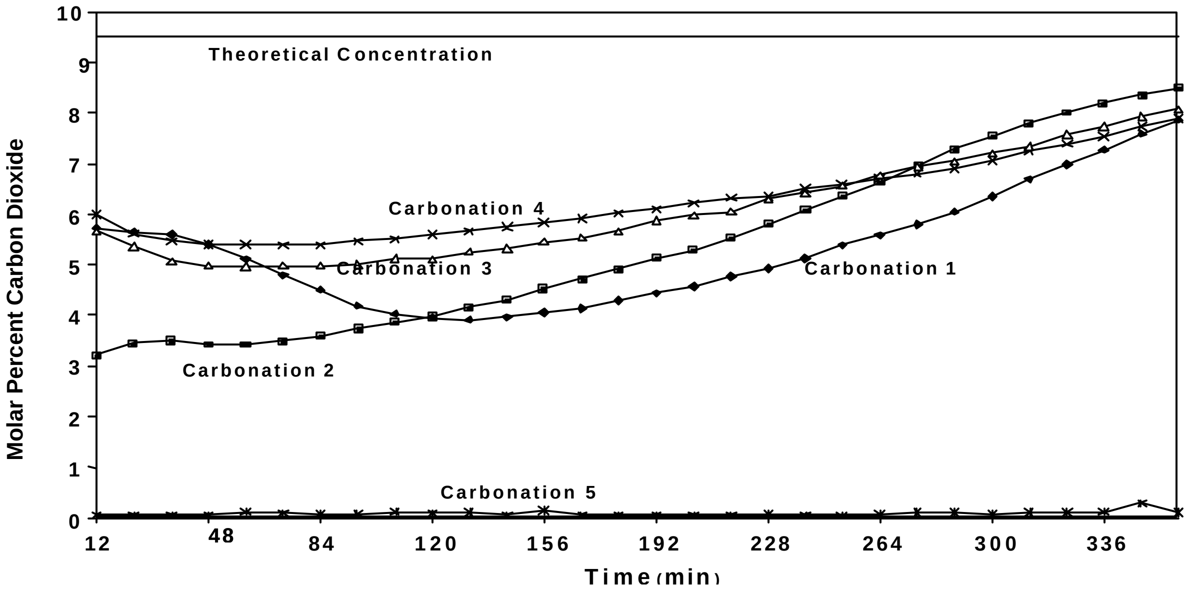

Figure 4. Carbon dioxide concentration of product gas from 5-cycle fixed bed test using SBC#3.

The percent CO_2 removal in the third sample of the first four cycles (based on the questionable data of Figure 4) increased from about 45% in cycle 1 to 65% in cycle 2, then decreased to 50% in cycle 3 and to 45% in cycle 4. The total quantity of CO_2 removed at the end of the 6-hour test ranged from 0.068 mols in cycle 3 to 0.088 mols in cycle 1. These values correspond to from 75% to almost 100% conversion of sorbent based on a product of Wegscheider's salt.

4.2 Thermogravimetric Analysis Testing at RTI

4.2.1 Testing of Additional Sodium Carbonate and Trona Materials

Two sodium carbonate materials were tested this quarter, in an attempt to identify active sorbents with good attrition resistence. A commercial grade dense ash sodium carbonate produced by General Chemical Company was dried in helium at 150EC and then exposed to an atmosphere of 6.2% water vapor and 7.5% carbon dioxide. This material was found to be practically unreactive, gaining only about 0.2% in weight over the course of 60-minutes. Data are shown in Figure 5.

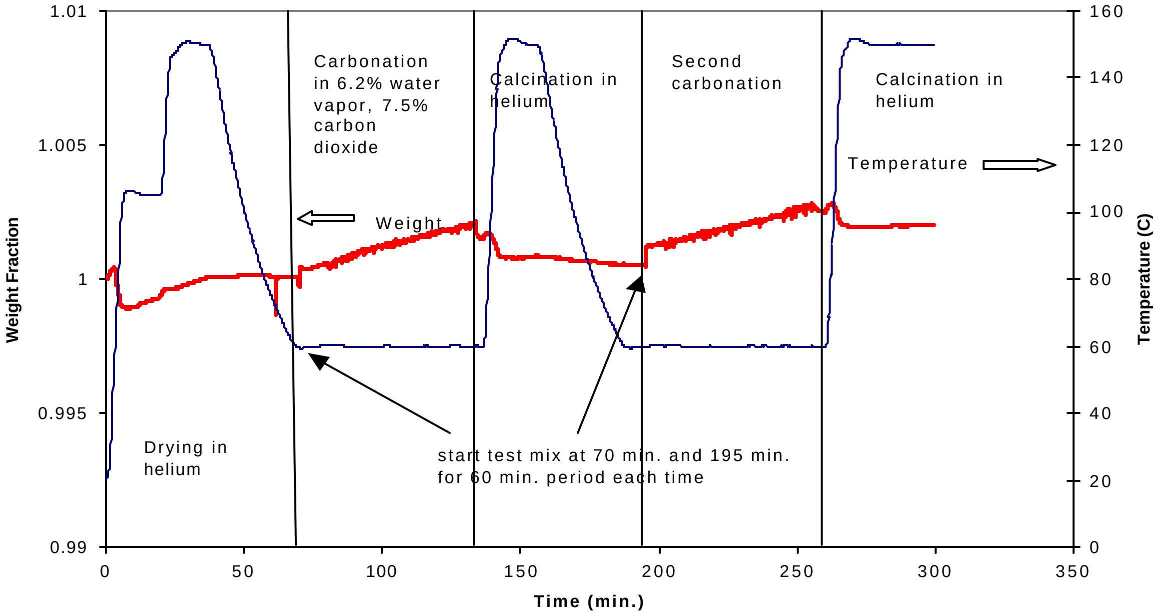

Figure 5. TGA of general chemical sodium carbonate (dense ash) Lot # E2315177

A second sodium carbonate material, natural light low density soda ash, also produced by General Chemical Company was predried and tested in a similar carbonation atmosphere. This material was similarly unreactive, gaining less than 0.5% in weight in a 60-minute test. Data are shown in Figure 6.

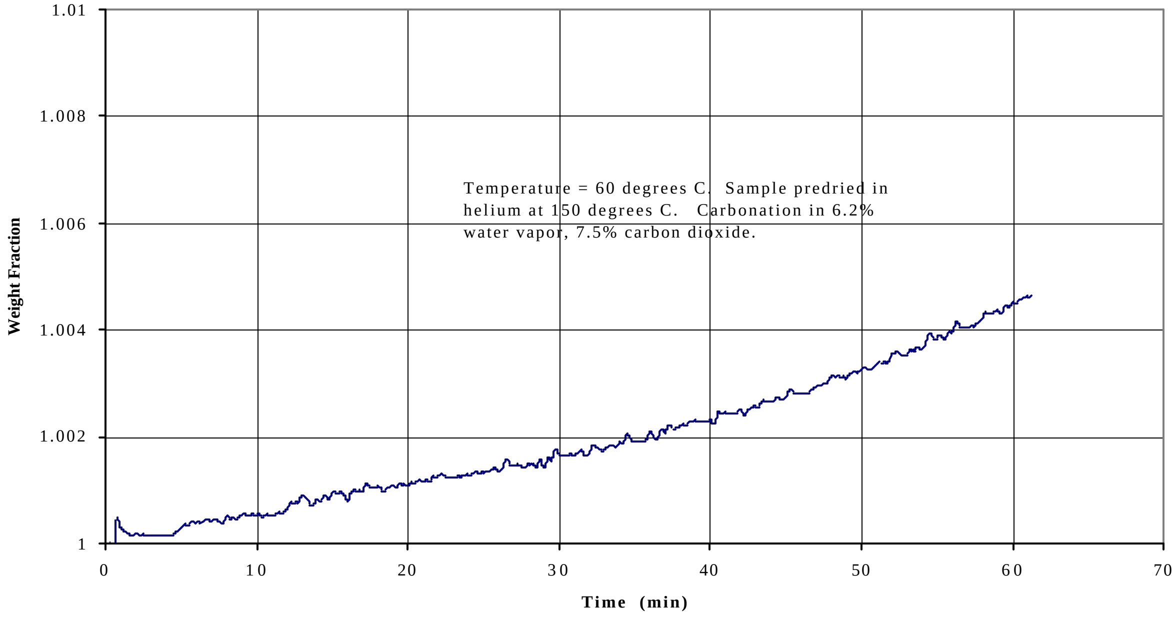

Figure 6. Carbonation of general chemical sodium carbonate (Natural Light Low Density Soda Ash Lot #E3005NL).

Two sodium sesquicarbonate materials were also tested this quarter. A commercial grade sodium sesquicarbonate produced by FMC was subjected to a two cycle test. Data are shown in Figure 7. The material was initially calcined (converted to sodium carbonate) in helium. Calcination was complete at 120EC; this was confirmed by raising the temperature to 150EC. Calcination weight loss was 28% which is approximately equal to the stoichiometric weight loss of 29.6%. The sodium carbonate was then carbonated in an atmosphere of 6.2% water vapor/7.5% carbon dioxide at 60EC and gained 17% in weight in one hour (compared to a weight gain of 58% for stoichiometric conversion to sodium bicarbonate). The material was rapidly and completely calcined to its baseline weight. A second carbonation resulted in a weight gain of 11%, representing a declining carbonation activity.

A second sodium sesquicarbonate material, unrefined trona, produced by Church and Dwight was tested by the same procedure as the FMC material. These data are shown in Figure 8. This material was slightly more active, gaining 19% and 16% in weight in the first and second carbonation cycles. The second calcination did not result in a weight loss to the baseline weight, suggesting that more severe calcination conditions might be needed. While neither of the sesquicarbonate materials tested this quarter resulted in sorbents more active than calcined SBC#3, they may offer advantages in terms of attrition resistence.

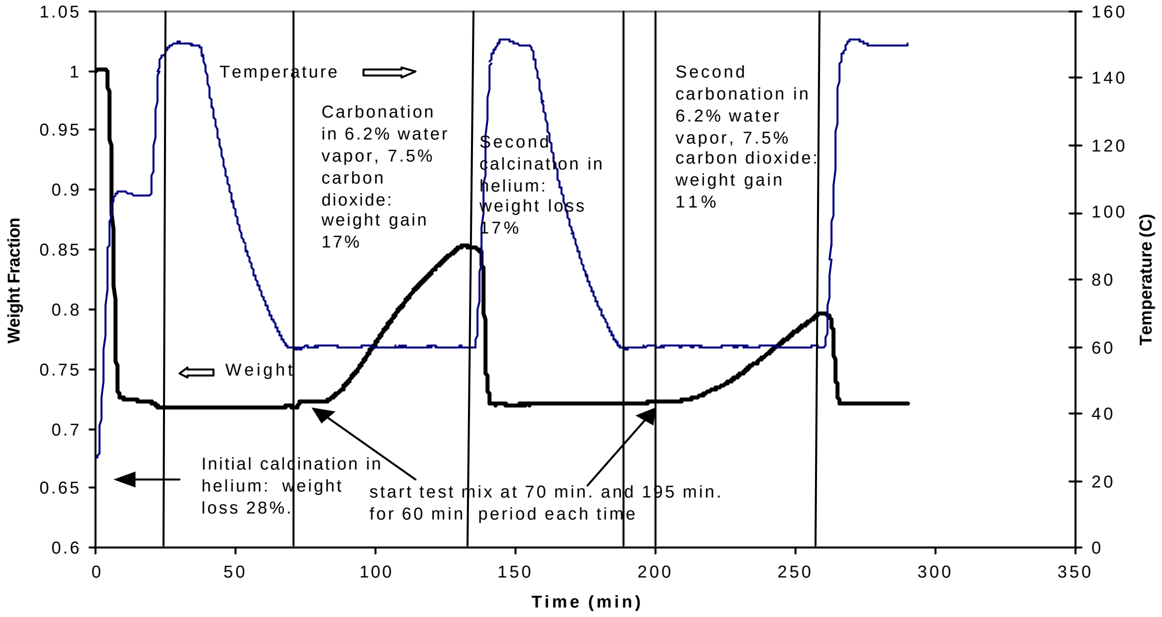

Figure 7. TGA of FMC "Sesqui"--[Sodium Sesquicarbonate (lot # 0325032800B)].

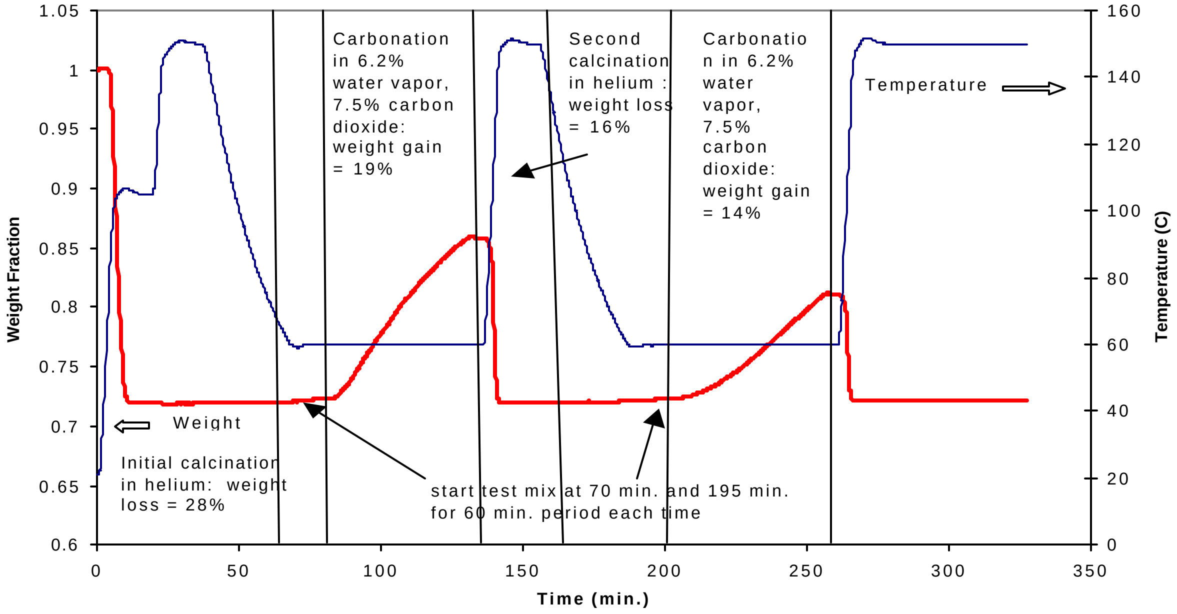

Figure 8. TGA of Church and Dwight SQ-810 Natural Sodium Sesquicarbonate (unrefined trona): Lot # 3020500150.

4.2.2 Testing of Supported Sodium Carbonate Sample

Another batch of spray-dried 40% supported sodium carbonate was prepared this quarter in an attempt obtain improved activity and attrition resistence. This material (sample 050603-2) was predried in helium and subjected to a two-cycle TGA test. In the initial carbonation in 6.2% water vapor/7.5% carbon dioxide, a very rapid weight gain of about 2% was observed and total weight gain over 60 minutes was 9.5% (equivalent to 24% of the active sorbent weight). During subsequent calcination in helium at 150EC, the material released about 90% of the carbonation weight gain. Performance in the second cycle was similar to that observed in the first cycle. Data from this test are shown in Figure 9.

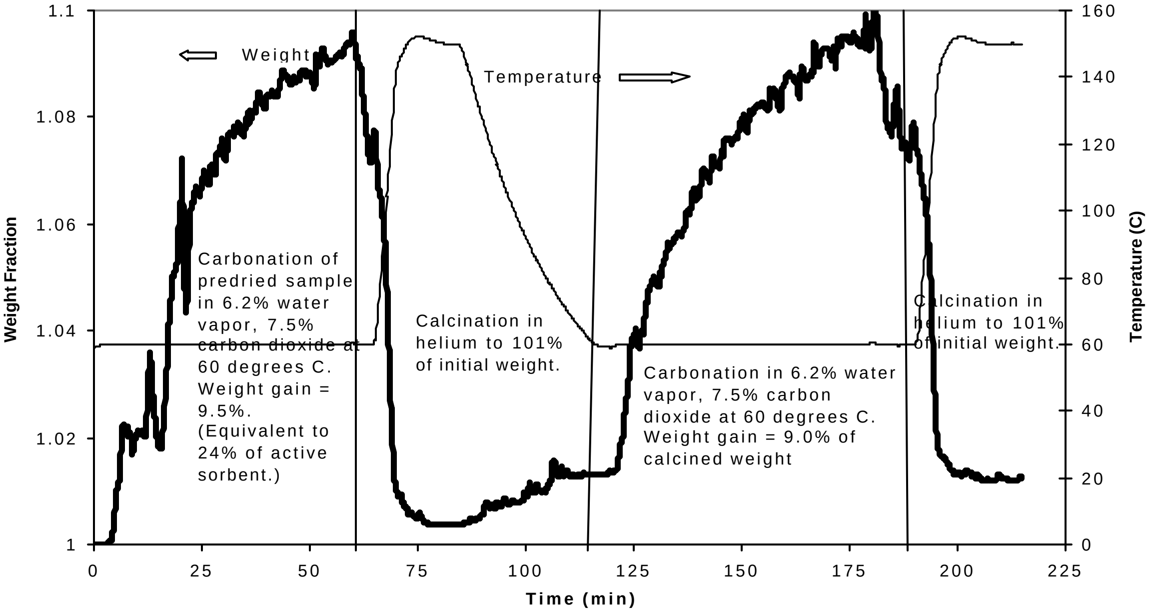

Figure 9. TGA of RTI sample # 050603-2 supported 40% sodium carbonate.

4.3 Physical Properties of Supported Materials

Three spray-dried supported sorbent materials were analyzed this quarter. Results are shown in Table 2.

Table 2. Physical Properties of Supported Sorbents

Sorbent	**20% sodium carbonate**	**40% sodium carbonate**	**40% sodium carbonate**
Sample Number	042503-2	042503-4	050603-2
BET Surface Area m^2/g	33.02	9.38	10.72
Compact Bulk Density g/cc	0.56	0.78	0.76
Total Intrusion Volume ml/g	n/a	0.3485	0.4075
Total Pore Area m^2/g	n/a	28.475	32.331
Median Pore Diameter (volume) Å	n/a	5922	5883
Median Pore Diameter (area) Å	n/a	74	76
Median Pore Diameter (4V/A) Å	n/a	490	504
Bulk Density g/ml	n/a	1.134	1.010
Skeletal Density g/ml	n/a	1.875	1.717
Porosity %	n/a	39.51	41.17

n/a = not determined

4.4 Estimation of Process Energy Requirements

One of the most important factors that, in part, determines the increased costs and the loss of power generation efficiency for a coal fired power plant due to incorporating CO_2 removal versus a power plant without CO_2 removal is the energy requirement for CO_2 sorbent regeneration. An idea of the energies involved in CO_2 removal can be obtained by comparing coal fired power plants with and without CO_2 removal. Such a comparison is shown in Table 3. Table 3 was constructed using data from a comprehensive DOE report prepared by EPRI (2000).

Table 3 compares the process energy requirements for Case 7A and 7C from the EPRI Report (2000). Case 7C is a base case for a coal fired power plant without CO_2 removal against which other coal fired power plants using various CO_2 removal alternatives can to be compared. Case 7A is similar to Case 7C except in Case 7A approximately 90% of the CO_2 in the flue gas is removed using an oxygen-inhibited MEA scrubbing process. As shown in Table 3, the gross plant power production is substantially reduced in Case 7A as compared to the base case. The reason for this is that the regeneration of the CO_2-rich MEA scrubbing solution in Case 7A utilizes low pressure steam that is not available for power generation as it is in the base case, Case 7C. Also, Table 3 reveals several other

Table 3. Process Energy Requirements for Coal Fired Power Plants with and without CO_2 Removal

CASE	**EPRI Case 7A Coal Fired Power Plant with MEA CO_2 Removal**	**EPRI Case 7C Coal Fired Power Plant without CO_2 Removal**
GROSS POWER SUMMARY, kWe		
Steam Turbine Power	408,089	498,319
Generator Loss	(5,835)	(7,211)
Gross Plant Power	402,254	491,108
AUXILIARY LOAD SUMMARY, kWe		
Coal Handling and Conveying	390	390
Limestone Handling & Reagent	920	920
Preparation	1,860	1,860
Pulverizers	1,670	1,670
Ash Handling	1,220	1,220
Primary Air Fans	970	970
Forced Draft Fans	19,880	5,050
Induced Draft Fans	100	100
SCR	50	50
Seal Air Blowers	1,000	1,000
Precipitators	3,450	3,450
FGD Pumps and Agitators	300	590
Condensate Pumps and Agitators	3,090	2,670
Boiler Feed Water booster Pumps	2,000	2,000
Miscellaneous Balance of Plant	400	400
Steam Turbine Auxiliaries	1,950	3,540
Circulating Water Pumps	1,110	2,030
Cooling Tower Fans	1,940	N/A
MEA Unit	29,730	N/A
CO_2 Compressor	930	1,140
Transformer Loss	72,730	29,050
Total Auxiliary Power Requirement		
NET PLANT POWER, kWe	329,294	462,058
PLANT EFFICIENCY		
Net Efficiency, % HHV	28.9%	40.5%
Net Heat Rate, kJ/kWh (Btu/kWh) (HHV)	12,463 (11,816)	8,882 (8,421)

For Case 7A: 90% CO_2 Removal
For all cases: Heat Input = 1,140,155 kW_{heat}(HHV)

power losses for the power plant that incorporates CO_2 removal in comparison to the base case. The major differences in power consumption in the auxiliary unit operations for the base case power plant (in comparison to the plant that incorporates CO_2 removal) are the power consumed in the Induced Draft Fans and the power required for CO_2 compression. The increased power consumption for the Induced Draft Fans in Case 7A over the base case, Case 7C, is due to the power required to overcome the flue gas pressure drop in the MEA scrubber. As shown in Table 3 for Case 7A, the power requirement for CO_2 compression is quite substantial.

Table 3 shows that, by far, the greatest loss of Net Plant Power when comparing the two cases is due to the reduction of power generated by the steam turbines as a result of using low-pressure steam to regenerate the MEA scrubbing solution as described above. Thus the efficiency of a coal fired power plant, which incorporates CO_2 removal by MEA solution, is highly dependent on the energy required to regenerate the MEA scrubbing solution. Unfortunately, in two recently published studies that were sponsored by DOE, there is a large difference in the heat required to regenerate the oxygen-inhibited MEA scrubbing solution. In the EPRI (2000) study the regeneration heat is 71,140 Btu per lbmol CO_2 captured from the flue gas and in the other study, carried out by Alstom Power (2001), the regeneration heat requirement is 103,400 Btu/lbmol CO_2. The effects of these two regeneration heats on thermal efficiencies of a coal fired power plant are shown in Table 4.

Table 4 shows that regeneration heats of 71,140 and 103,400 Btu/lbmol CO_2 give thermal efficiencies for the power plants of 28.9 and 25.4%, respectively. This is a very significant effect.

In Table 4, the estimated thermal efficiency of a coal fired power plant using RTI's Na_2CO_3-based CO_2 capture process is compared to EPRI Case 7A and to Case 7A with the loss of steam turbine power calculated using a MEA regeneration heat duty of 103,400 Btu/lbmol CO_2. The thermal efficiency of the power plant using RTI's dry CO_2 removal process compares favorably with the power plants using the oxygen inhibited MEA-based CO_2 removal process. Similarly, as in the MEA-based CO_2 removal process, the heat requirement for the regeneration of the Na_2CO_3 based dry CO_2 sorbent is critical to determining the resulting thermal-efficiency of a power plant using this technology. In Table 4, it was assumed that the heat requirement for regenerating RTI's Na_2CO_3 based dry CO_2 sorbent was approximately 60,000 Btu/lbmol CO_2. This figure is very close to the theoretical value that would be expected based on the thermodynamics of the carbonization of sodium carbonate to Wegscheider's salt. As will be shown below, the exact regeneration heat requirement for RTI's Na_2CO_3-based dry CO_2 removal process will depend on the operating conditions of the process. Two of the major factors affecting the regeneration heat requirement are the Na_2CO_3 loading on the sorbent and the Na_2CO_3 utilization.

Table 4. Effect of Heat Requirement for Sorbent Regeneration of Thermal Efficiency

CASE	**Heat Requirement for CO_2 Regenerator Btu/lbmol CO_2**	**Gross Plant Power kW_e**	**Auxiliary Power Requirement kW_e**	**Net Plant Power kW_e**	**Plant Efficiency (HHV) %**
EPRI Base Case 7C, Coal Fired Steam Plant without CO_2 Removal	Not Applicable	491,108	29,050	462,058	40.5
EPRI Case 7A, Coal-Fired plant with O_2 inhibited MEA CO_2 Removal	71,140[E]	402,254	72,730	329,524	28.9
EPRI Case 7A Recalculated, Coal fired plant with O_2 inhibited MEA CO_2 Removal	103,400[A]	362,178	72,730	289,448	25.4
Coal fired plant with Na_2CO_3 - based dry CO_2 Removal	60,000	416,144	72,730	343,414	30.1

90% CO_2 Removal for Applicable Cases
For all cases: Heat input = 1,140,155 kW_{heat}(HHV)
[E] EPRI, Evaluation of Innovative Fossil Fuel Power Plants with CO_2 Removal, 2000
[A] Alstom Power Engineering Feasibility and Economics of CO_2 Capture on an Existing Coal Fired Power Plant 2001

In Table 4, each power plant alternative was assumed to have the same heat input, and for the power plants which incorporated CO_2 removal, the CO_2 removal efficiency was assumed to be 90%. Thus, for each of these plants the rate of CO_2 removal was the same. Given the regeneration heat requirement for the respective CO_2 removal processes, the rate at which heat is needed for the regeneration of the CO_2 absorbent can be calculated. Based on a thermal efficiency of converting heat from low pressure steam to shaft power in a turbine of 26.7%, the Gross Plant Power of the recalculated EPRI Case 7A shown in Table 4, and the power plant case that uses the RTI dry process for CO_2 removal was calculated. The auxiliary power requirements for these two cases were assumed to be the same as EPRI's Case 7A (as shown in Table 4). This assumption for the recalculated EPRI Case7A and the power plant using the RTI dry process may not be unreasonable because the major determinants of the auxiliary power requirements, as explained above, are: 1) the CO_2 compression power requirements which are the same for each power plant listed in Table 4 where CO_2 removal is applicable, and 2) the power required by the induced draft fans which might be similar for the MEA-based process and the Na_2CO_3-based dry CO_2 removal process, (although, it is anticipated, under more detailed analysis, that the dry process should have a lower pressure drop than the MEA-based CO_2 removal process which involves bubbling the flue gas through a height of liquid in a packed column). The power generation efficiency from low-pressure steam of 26.7% was calculated based on a comparison of EPRI's Cases 7A and 7C.

Based on the rough analysis described above and summarized in Table 4, the RTI Na_2CO_3-based dry CO_2 removal process may be capable of yielding an overall thermal efficiency for a power plant utilizing this CO_2 removal technology that is much higher than a power plant using an MEA-based CO_2 removal process.

The thermal efficiency that can be obtained for a power plant, which utilizes the RTI Na_2CO_3-based dry CO_2 removal process, is highly dependent on the heat requirement for regenerating the carbonized sorbent. To determine how this requirement depends on the operating conditions of the Carbonizer-Regenerator combination, the following model of the combination is developed.

A simplified flow diagram of the RTI process is shown in Figure 10. The main features of this process are as follows. Flue gas is fed to the bottom of the carbonizer where it is mixed with recycled and regenerated sorbent. The carbonizer and regenerator are both fast fluidized beds. In the carbonizer, CO_2 and water vapor react with Na_2CO_3 contained in the sorbent to produce Wegscheider's salt. At discrete points along the length of the carbonizer, liquid water is injected into the flue gas/sorbent mixture passing up the carbonizer. The injected water promotes the carbonization reaction by cooling the gas/solid mixture thus increasing the thermodynamic favorability of the carbonization reaction and also promotes the carbonization reaction by increasing the concentration of water vapor in the carbonizer. At the outlet of the carbonizer the treated flue gas and loaded sorbent are separated. At this point a fraction, f, of the loaded sorbent is split off to the bottom of the regenerator and the remainder of the loaded sorbent is recycled to the bottom of the carbonizer as shown in Figure 10. In the regenerator, the loaded sorbent is contacted by recycled sweep gas which contains both CO_2 and water vapor. The sorbent and sweep gas are heated. This regeneration heat is labeled "Q" on Figure 10. At the top of the regenerator, the regenerated sorbent and the sweep gas are separated. The regenerated sorbent is recycled to the bottom of the carbonizer. Most of sweep gas is recycled to the bottom of the regenerator and a bleed stream of CO_2 and water vapor is removed from the sweep gas loop for further processing to recover purified CO_2.

On Figure 10, several of the critical points within the CO_2 capture process have been numbered. These points are the inlet and outlets of the carbonizer and regenerator.

In the present development of a method to determine how the regenerator heat requirement, Q, depends on process operating conditions, total regeneration of the sorbent in the regenerator has been assumed. This implies that $X_c^{(4)} = 0$ where $X_c^{(4)}$ is the carbonate conversion at Point 4 on Figure 10.

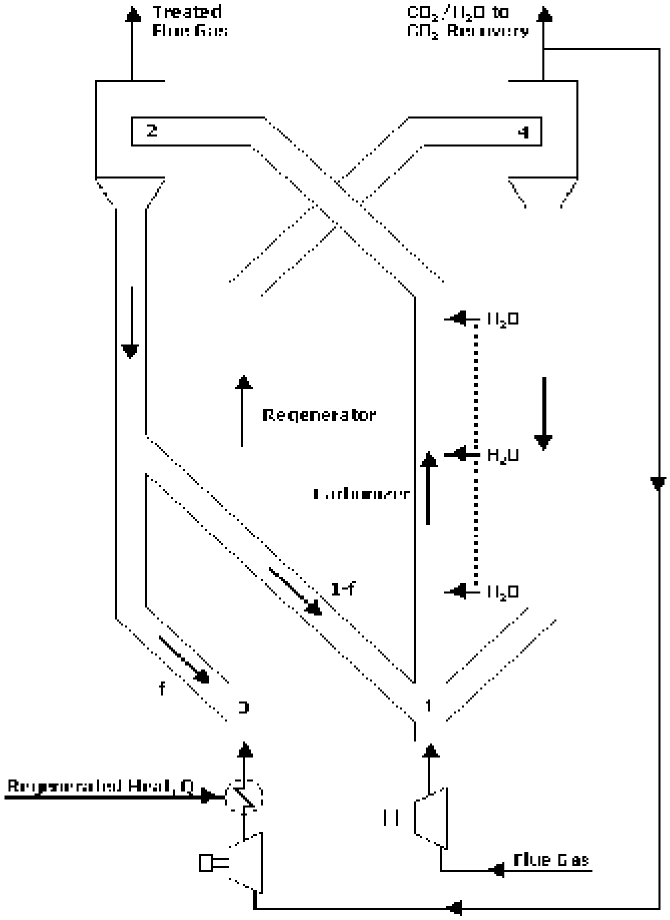

Figure 10. Simplified flow sheet for the RTI sodium carbonate based dry carbon dioxide capture process.

At any point in the process the flows of the various solids can be determined by

$$N_w^{(i)} = \frac{S_o^{(i)} W_c (1 - X_c^{(i)})}{106} \tag{7}$$

$$N_w^{(i)} = \frac{2}{5} \frac{S_o^{(i)} W_c (X_c^{(i)})}{106} \tag{8}$$

$$N_s^{(i)} = \frac{S_o^{(i)} (1 - W_c)}{183} \tag{9}$$

where $N_j^{(1)}$ is the mass flow rate of component j at the i^th point of the flow sheet, lbmol/hr, and C = Na_2CO_3, W = $Na_2CO_3 \cdot 3NaHCO_3$ and S = support material

$S_o^{(1)}$ is the mass flow rate sorbent flowing at point i if the conversion X_c was extrapolated back to zero, lb/hr,

W_c is the weight fraction Na_2CO_3 in the fresh sorbent,

and $X_c^{(1)}$ is the Na_2CO_3 conversion at point i.

Let f be the fraction of the circulating solids in the carbonizer outlet that are split off from the regenerator, then by material balance,

$$N_c^{(1)} = \underbrace{N_c^{(2)}(1 - f)}_{Na_2CO_3 \text{ not sent to Regenerator}} + \underbrace{fN_w^{(2)} \tfrac{5}{2}}_{Na_2CO_3 \text{ produced by Regeneration of Wegsalt}} + \underbrace{fN_c^{(2)}}_{Na_2CO_3 \text{ sent to Regenerator}} \tag{10}$$

or

$$N_c^{(i)} = N_c^{(2)} + fN_w^{(2)} \left(\tfrac{5}{2}\right). \tag{11}$$

Noting that

$$N_c^{(2)} = N_c^{(1)} - \tfrac{5}{3} M_{CO_2} \tag{12}$$

where M_{CO2} = moles of CO_2 absorbed in carbonizer, lbmol/hr. Substituting Equation 12 into Equation 11 and making use of Equation 8 gives

$$N_c^{(1)} = N_c^{(1)} - \tfrac{5}{3} M_{CO_2} + f \tfrac{5}{2} \left(\tfrac{2}{5}\right) \tfrac{S_o^2 W_c}{106} X_c^{(2)} \tag{13}$$

Noting that the sorbent support is conserved in the carbonizer, gives, by Equation 8

$$S_o^{(2)} = S_o^{(1)} \tag{14}$$

Simplifying Equation 13 gives

$$X_c^{(2)} = \frac{5}{3}\frac{M_{CO_2}(106)}{S_o^{(1)} W_c f} \tag{15}$$

The carbonate conversion, $X_c^{(2)}$ could be called the sorbent utilization since this the highest Na_2CO_3 conversion achieved in the carbonizer-regenerator system.

Based on the above equations, and given 1) the temperature of the solids leaving the carbonizer and regenerator, and 2) the temperature of the gas leaving the regenerator, a heat balance can be carried out around the regenerator section to determine the heat requirement, Q, for the regenerator.

Based on previous simulations of the regenerator carried out by RTI, it was found that the gas and solids leave the regenerator at approximately the equilibrium temperature, T_{eq}, for the Na_2CO_3 to Wegscheider's salt reaction based on the bulk gas CO_2 and water vapor partial pressures. Thus, the equilibrium temperature is given by the solution of

$$K[T_{eq}] = P_{CO_2} \bullet P_{H_2O} \tag{16}$$

where K[Teq] is the equilibrium constant for the Na_2CO_3-Wegscheider's salt reaction and is a function of temperature only,

and P_{CO2} and P_{H2O} are the partial pressures of CO_2 and water vapor in the bulk gas, respectively, atm.

Based on minimizing cooling and reheating of the regeneration sweep gas and as a consequence, minimizing the heat exchange equipment needed to do the cooling and reheating, the sweep gas is assumed to be a 50/50 mixture of CO_2 and water vapor. Under this assumption, using Equation 16 and assuming the total pressure in the regenerator is roughly 1 atm, gives an outlet temperature of the regenerator of about 225EF.

The outlet temperature of the solids leaving the carbonizer can be estimated assuming that the solids are in equilibrium with the gas leaving the carbonizer and that the liquid water injection is roughly equal to the amount needed to balance the heat release by the carbonization by the evaporation of the water. Thus the temperature of the solids leaving the carbonizer will be, roughly, those shown in Table 5 for a flue gas containing 12.82% CO_2 and 15.78% H_2O at the inlet of the carbonizer.

Table 5. Estimated exit temperature for the carbonizer solids

Percent CO_2 Removal	Estimated H_2O injection lbmol/lbmol flue gas	Estimated Solid temperature at Carbonizer exit, EF
0	0	186.7
12.5	0.0529	187.2
25.0	0.1058	186.9
50.0	0.2116	184.0
67.5	0.2645	181.1
75.0	0.3174	176.5

Since RTI's target CO_2 removal is 50%, and the temperature of the solids leaving the carbonizer (for CO_2 removal less than 50%) is greater than the outlet temperature at the 50% CO_2 removal level as (shown in Table 3), then using an outlet solid temperature of 184EF should yield a conservative estimate of the regenerator heat requirement for CO_2 removal levels of less than or equal to 50%.

Carrying out a heat balance around the regenerator and ignoring work done to compress the sweep gas gives

$$\begin{aligned} & N_c^{(2)} f\, h_c^{184} + N_w^{(2)} f\, h_w^{184} + f N_s^{(2)}\, h_s^{184} + Q \\ & - M_{CO_2}\left[h_{CO_2}^{225} + h_{H_2O}^{225}\right] - N_c^{(4)}\, h_c^{225} \\ & - N_s^{(4)}\, h_s^{225} = O \end{aligned} \tag{17}$$

where h_i^T is the enthalpy of component i at temperature T (EF) relative to the elements at standard conditions, Btu/lbmol

and

Q is heat added to the Regenerator system, Btu/hr.

Substituting Equations 7, 8, 9 and 14 into Equation 17 and noting, that by the conservation of sorbent support,

$$S_o^{(4)} = f\, S_o^{(1)} \tag{18}$$

gives

$$f\,\frac{S_o^{(1)}W_c}{106}(1-X_c^{(2)})\;h_c^{184}+f\frac{S_o^{(1)}W_c}{106}\,X_c^{(2)}\,\frac{2}{5}h_w^{184}+f\frac{S_o^{1}(1-W_c)}{183}\,h_s^{184}$$

$$+\;Q-M_{CO_2}\left[h_{CO_2}^{225}+h_{H_2O}^{225}\right]-f\;\frac{S_o^{(1)}W_ch_c^{225}}{106} \qquad (19)$$

$$-\,f\;\frac{S_o^{(1)}(1\text{-}\,W_c)h_s^{225}}{183}\;=\;O$$

Dividing each term of Equation 19 by the CO_2 absorption rate, M_{CO2}, and making use of Equation 15 gives

$$\frac{5}{3}\frac{(1-X_c^{(2)})}{X_c^{(2)}}h_c^{184}+\frac{2}{3}h_w^{184}+\frac{5}{3}\frac{(106)}{183}\frac{(1-W_c)}{X_c^{(2)}W_c}h_s^{184}$$

$$+\;Q-\left[h_{CO2}^{225}+H_{H2O}^{225}\right]-\frac{5}{3X_c^{(2)}}h_c^{225} \qquad (20)$$

$$-\,\frac{5}{3}\frac{(106)}{183}\frac{(1-W_c)}{X_c^{(2)}W_c}h_s^{225}\;=\;O$$

The enthalpies listed in Equation 20 can be evaluated by standard techniques using the standard enthalpies of formation given by Vanderzee (1982), for every component except the support material (which was taken from Knacke et al. (1991), and using heat capacities given by Knacke et al. (1991), for each component except Wegscheidner's salt which was taken from Vanderzee (1982). The enthalpies used to evaluate Equation 20 are listed in Table 6.

Table 6. Enthalpies of formation relative to the elements at standard condition for various components at 184 and 225EF

Symbol	Component	Enthalpy Btu/lbmole	
		T = 184EF	T = 225EF
$h_{CO_2}^T$	CO_2		!167840
$h_{H_2O}^T$	H_2O(g)		!102830
h_c^T	Na_2CO_3	!482740	!481570
h_w^T	Na_2CO_3C$3NaHCO_3$	!1700400	
h_s^T	Support	!887580	!886220

Using the data given in Table 4 and evaluating each term in Equation 20 gives

$$\frac{Q}{M_{CO_2}} = 58360 + \frac{637}{X_c^{(2)}} + \frac{1313}{X_c^{(2)} W_c} \qquad (21)$$

Equation 21 provides a quick method to determine the heat that must be supplied to the regenerator. For example, using RTI's present target for Na_2CO_3 loading on the sorbent or

$$W_c = 0.4 \qquad (22)$$

and expected sorbent utilization,

$$X_c^{(2)} = 0.25 \qquad (23)$$

Equation 21 gives the regenerator heat duty as

$$\frac{Q}{M_{CO_2}} = 74040 + \frac{\text{Btu}}{\text{lbmol } CO_2} \qquad (24)$$

The heat duty is roughly 25% greater than the regenerator heat duty assumed in the construction of Table 4 for the case of RTI's Na_2CO_3-based dry CO_2 capture process. The heat duty of 74040 Btu/lbmol CO_2 calculated using Equation 21 is 75% of the oxygen inhibited MEA scrubbing solution regeneration heat given by Alstom Power (2001) and is about equal to that given by EPRI (2000). Thus, the improvement in power plant performance using the RTI Na_2CO_3-based dry CO_2 capture process versus a oxygen-inhibited MEA based CO_2 capture process cannot be made until a more detailed engineering design of the RTI process is complete and the discrepancy between the heat required to regenerate oxygen inhibited MEA solution given by EPRI and Alstom Power is resolved.

Without a more detailed engineering design of the RTI CO_2 capture process, Equation 21 makes it clear that areas of research on the RTI process should be the maximization of the Na_2CO_3 loading on the sorbent while maintaining structural integrity and durability and the investigation of methods of sorbent preparation that might lead to enhanced Na_2CO_3 utilization.

4.5 Other Project Activities

RTI and LSU presented a paper at the Second Annual Conference on Carbon Sequestration in Alexandria, Virginia on May 6, 2003. RTI and LSU participated in a program review meeting in June, 2003.

5.0 CONCLUSIONS AND FUTURE WORK

Multi-cycle fixed bed tests suggest that SBC#1 behaves similarly to SBC#3, in that carbonation activity increases after the second calcination and does not decline in cycles 2 through 5.

TGA testing indicates that low density sodium carbonate and dense ash sodium carbonate exhibit relatively little carbonation activity. In addition two different sodium sesquicarbonate materials were tested and found to be less active after calcination than calcined SBC.

Different data sources lead to different estimates of energy requirements for liquid absorption processes based on monoethylamine materials. Mathematical modeling of the dry sorbent process indicates that, for supported sorbents, the amount of active sorbent loaded on the support is critical to the energy requirements for the process.

During the next quarter, LSU will improve the fixed bed reactor and gas analysis systems. RTI will conduct fluid bed tests on the most recent batch of supported sorbent. Church and Dwight will complete a preliminary economic analysis of the process.

6.0 REFERENCES

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